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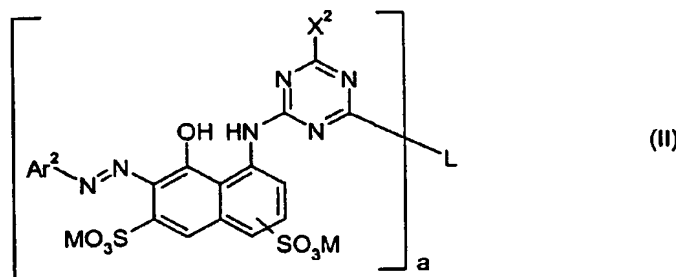
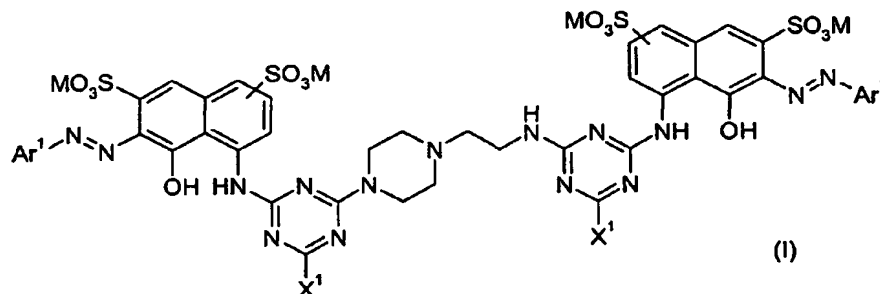
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(54) Title: DYE MIXTURES OF FIBRE-REACTIVE AZO DYES AND USE THEREOF FOR DYEING MATERIAL CONTAIN-  
ING HYDROXY- AND/OR CARBOXAMIDO GROUPS



(57) Abstract: Mixtures of fibre reactive dyes comprising one or more dyestuffs of the formula (I) and one or more dyestuffs of the general formula (II) wherein Ar<sup>1</sup>, Ar<sup>2</sup>, X<sup>1</sup>, X<sup>2</sup>, L and M are as defined in claim 1.



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5 Dye Mixtures Of Fibre-Reactive Azo Dyes And Use Thereof For Dyeing  
Material Containing Hydroxy- And/Or Carboxamido Groups

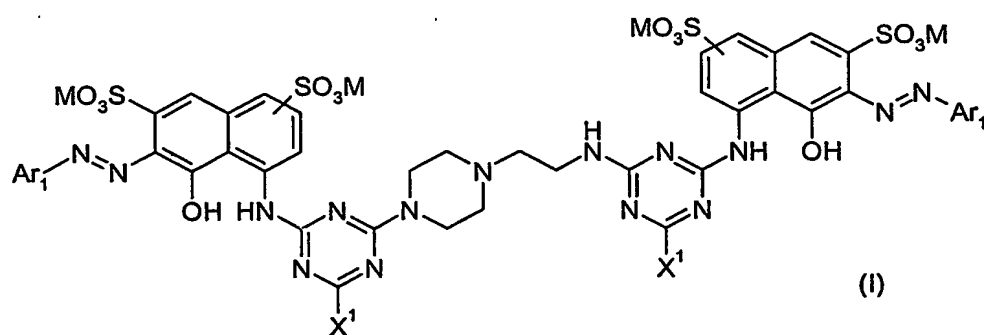
The present invention relates to the field of fibre-reactive dyes.

10 Dyestuffs containing chromophores linked via a piperazine type linking unit  
are known from literature and are described for example in EP-A-0126265,  
EP-A-0693538, WO99/05224 and WO00/08104.

The inventors of the present invention have surprisingly found that mixtures  
15 of dyestuffs of the general formula (I) and dyestuffs of the general formula  
(II) give excellent application properties on cellulose containing material,  
especially high levels of solubility in water or salt solution, high fixation  
degrees, ease of washing out the unfixed dyestuff, good fastness to light  
and water as well as robustness to process variables.

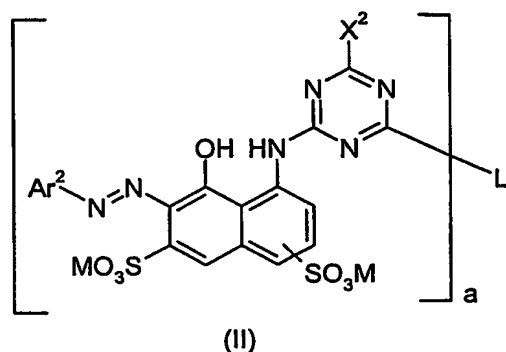
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The present invention claims mixtures of fibre reactive dyes comprising one  
or more dyestuffs of the formula (I)



25

and one or more dyestuffs of the general formula (II)



where

$X^1, X^2$  independently are a labile atom or group;

5  $Ar^1$  is an aromatic residue substituted by at least one  $-SO_3M$  group,

$M$  is hydrogen or alkali metal, especially sodium,

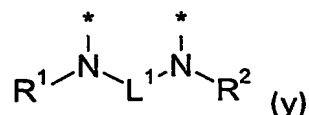
$Ar^2$  is an aromatic radical substituted with at least one  $-SO_3M$  group,

$a$  is 1 or 2

wherein,

10 if  $a$  is 2

$L$  is a divalent radical typically of the form (y)



where

15  $R^1$  and  $R^2$  are independently hydrogen,  $C_1$ - $C_4$  alkyl optionally substituted by  $-OR$ ,  $-SR$ ,  $-SO_3M$ , or  $-X$ ,

or a phenyl group optionally substituted by a sulfonic acid group,  $-OR$ ,  $-C_1$ - $C_4$  alkyl, or  $-NR'COR$

20  $L^1$  is alkylene or arylene optionally substituted by a sulfonic acid group,  $-OR$ ,  $-C_1$ - $C_4$  alkyl or  $-NR'COR$ ,  $-COOR$

wherein  $R$  and  $R'$  are independently hydrogen or  $C_1$ - $C_4$  alkyl and  $X$  is halogen

or  $R^1$  and  $R^2$  are independently optionally substituted alkyl, or

$L$  is aminoethylpiperazine, under the proviso that if  $L$  is

25 aminopiperazine,  $Ar^1$  and  $Ar^2$  are different or

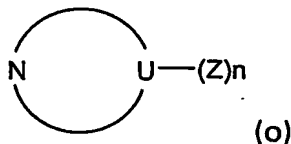
if a is 1

L is a monovalent radical  $-NR^3R^4$ ,  $-SR^3$  or  $-OR^3$

where

$R^3$  and  $R^4$  have one of the meanings of  $R^1$  and  $R^2$  or for -

5  $NR^3R^4$ ,  $R^3$  and  $R^4$  can form a cyclic structure of the form (o)



where

10 U is a  $C_4$ -  $C_6$  alkyl residue optionally substituted by a substituent of formula Z and optionally interrupted by heteroatoms or heteroatom-containing groups such as - O-, -  $NR^1$ ,

n is 1, 2 or 3 and

15 Z is hydrogen, optionally substituted  $C_1$ - $C_4$  alkyl,  $-OR^5$ , -  $CO_2R^5$ ,  $-COR^5$  and

$R^5$  is hydrogen, optionally substituted  $C_1$ - $C_4$  alkyl, optionally substituted vinyl, optionally substituted phenyl.

20  $(C_1$ - $C_4$ )-alkyl groups may be straight-chain or branched and are preferably for example methyl, ethyl, n-propyl, i-propyl or n-butyl. Substituted alkyl groups are preferably substituted by hydroxyl,  $(C_1$ - $C_4$ )-alkoxy, halogen or carboxyl groups. Substituted vinyl groups are for example -  $C(CH_3)=CH_2$  or -  $CH=CHCOOH$ , substituted phenyl groups are for example phenyl substituted  
25 by -  $COOH$ , or -  $SO_3M$ .

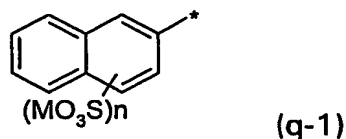
Preferred embodiments of the invention are mixtures of one or more dyestuffs of the general formula (I) and one or more dyestuffs of the general formula (II)

30 where

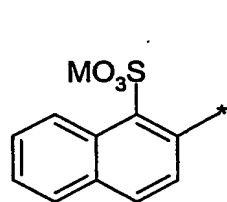
$X^1$  and  $X^2$  are independently chlorine, fluorine or 3 or 4-carboxypyridinium  
especially preferred is chlorine,

$Ar^1$  and  $Ar^2$  are independently a naphthyl residue substituted by at least one  
sulfo group (q-1)

5

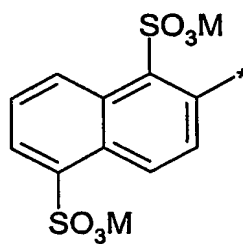


where n is 1 to 3, especially preferred (q-11) or (q-12)



(q-11)

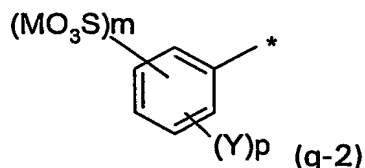
or



(q-12)

10

or are a phenyl residue substituted by at least one sulfo group (q-2)



wherein

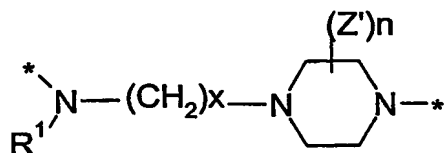
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$m$  is 1 or 2

$p$  is 1 or 2

$Y$  is independently hydrogen, halogen,  $R^5$ ,  $OR^5$ ,  $SR^5$ ,  $NHCOR^5$ ,  
where  $R^5$  is as defined above, especially preferred  $Y$  is methyl.

20 When  $a$  is 2  $L^1$  is preferred to be an optionally substituted phenylene or an  
alkylene residue optionally substituted or optionally interrupted by  
heteroatoms or heteroatom containing groups, wherein  $L^1-N-R^1$  or  $L^1-N-R^2$   
may contain a cyclic structural feature such as



where  $n$  and  $R^1$  are as defined above and  $x$  is 2 to 5 and  $Z'$  has one of the meanings of  $Z$ .

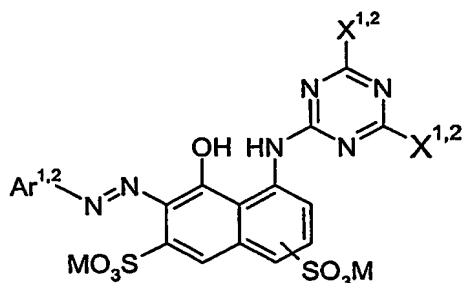
When  $a$  is 1  $L$  is preferably morpholine or  $N$ -Methylsulfanilic acid.

5

The dyestuffs of the formula (I) are contained in the mixture in quantity of 1 % by weight to 99 % by weight preferably in a mixing ration of 10 % by weight to 90 % by weight and the dyestuffs of the formula (II) are contained in the mixture in a mixing ratio of 99 % by weight to 1 % by weight,

10 preferably in a mixing ratio of 90 % by weight to 10 % by weight.

Dyestuff mixtures according to the invention can be obtained upon reacting chromophores of formula (III)



(III)

15

with an appropriate mixture of 2-aminoethylpiperazine and a diamine  $H-L-H$ , or amine  $H-L$ , wherein  $L$  is as defined above, followed by precipitation using methylated spirits and conventional filtration.

20

The dyestuffs of the present invention can be present as a preparation in solid or liquid (dissolved) form. In solid form they generally contain the electrolyte salts customary in the case of water-soluble and in particular fibre-reactive dyes, such as sodium chloride, potassium chloride and sodium

- sulfate, and also the auxiliaries customary in commercial dyes, such as buffer substances capable of establishing a pH in aqueous solution between 3 and 8, such as sodium acetate, sodium borate, sodium bicarbonate, sodium citrate, sodium dihydrogenphosphate and disodium
- 5 hydrogenphosphate, small amounts of siccatives or, if they are present in liquid, aqueous solution (including the presence of thickeners of the type customary in print pastes), substances which ensure the permanence of these preparations, for example mold preventatives.
- 10 In general, the dyestuff mixtures of the present invention are present as dye powders containing 10 to 80% by weight, based on the dye powder or preparation, of a strength-standardizing colorless diluent electrolyte salt, such as those mentioned above. These dye powders may additionally include the aforementioned buffer substances in a total amount of up to 10%, based
- 15 on the dye powder. If the dye mixtures of the present invention are present in aqueous solution, the total dye content of these aqueous solutions is up to about 50 % by weight, for example between 5 and 50% by weight, and the electrolyte salt content of these aqueous solutions will preferably be below 10% by weight, based on the aqueous solutions. The aqueous solutions
- 20 (liquid preparations) may include the aforementioned buffer substances in an amount which is generally up to 10% by weight, for example 0.1 to 10% by weight, preference being given to up to 4% by weight, especially 2 to 4% by weight.
- 25 The dyestuff mixtures of the instant invention are reactive dyestuffs suitable for dyeing and printing hydroxy- and/or carboxamido-containing fibre materials by the application and fixing methods numerous described in the art for fibre-reactive dyes. They provide exceptionally strong and economic shades. Such dyes especially when used for exhaust dyeing of cellulosic
- 30 materials can exhibit excellent properties including build-up, light-fastness, high levels of solubility in water or salt solution, high fixation degrees, ease of washing out the unfixed dyestuff, as well as robustness to process

variables.

They are also wholly compatible with similar dyes designed for high temperature (80-100°C) application to cellulosic textiles, and thus lead to highly reproducible application processes, with short application times.

The present invention therefore also provides for use of the inventive dyestuffs for dyeing and printing hydroxy- and/or carboxamido-containing fibre materials and processes for dyeing and printing such materials using a dyestuff according to the invention. Usually the dyestuff is applied to the substrate in dissolved form and fixed on the fibre by the action of an alkali or by heating or both.

Hydroxy-containing materials are natural or synthetic hydroxy-containing materials, for example cellulose fiber materials, including in the form of paper, or their regenerated products and polyvinyl alcohols. Cellulose fiber materials are preferably cotton but also other natural vegetable fibers, such as linen, hemp, jute and ramie fibres. Regenerated cellulose fibers are for example staple viscose and filament viscose.

Carboxamido-containing materials are for example synthetic and natural polyamides and polyurethanes, in particular in the form of fibers, for example wool and other animal hairs, silk, leather, nylon-6,6, nylon-6, nylon-11, and nylon-4.

Application of the inventive dyestuffs is by generally known processes for dyeing and printing fiber materials by the known application techniques for fibre-reactive dyes. The dyestuffs according to the invention are highly compatible with similar dyes designed for high temperature (80-100°C) applications and are advantageously useful in exhaust dyeing processes.

Similarly, the conventional printing processes for cellulose fibers, which can either be carried out in single-phase, for example by printing with a print



paste containing sodium bicarbonate or some other acid-binding agent and the colorant, and subsequent steaming at appropriate temperatures, or in two phases, for example by printing with a neutral or weakly acid print paste containing the colorant and subsequent fixation either by passing the printed material through a hot electrolyte-containing alkaline bath or by overpadding with an alkaline electrolyte-containing padding liquor and subsequent batching of this treated material or subsequent steaming or subsequent treatment with dry heat, produce strong prints with well defined contours and a clear white ground. Changing fixing conditions has only little effect on the outcome of the prints. Not only in dyeing but also in printing the degrees of fixation obtained with dye mixtures of the invention are very high. The hot air used in dry heat fixing by the customary thermofix processes has a temperature of from 120 to 200°C. In addition to the customary steam at from 101 to 103°C, it is also possible to use superheated steam and high pressure steam at up to 160°C.

The inventive dyestuffs can in addition be used to produce inks useful for printing the substrates described above, for example textiles, especially cellulosic textiles, and paper. Such inks can be used in all technologies, for example conventional printing, ink-jet printing or bubble-jet printing (for information on such printing technologies see for example Text. Chem. Color, Volume 19(8), pages 23 ff and Volume 21, pages 27 ff).

Acid-binding agents responsible for fixing the dyes to cellulose fibers are for example water-soluble basic salts of alkali metals and of alkaline earth metals of inorganic or organic acids, and compounds, which release alkali when hot. Of particular suitability are the alkali metal hydroxides and alkali metal salts of weak to medium inorganic or organic acids; the preferred alkali metal compounds being the sodium and potassium compounds. These acid-binding agents are for example sodium hydroxide, potassium hydroxide, sodium carbonate, sodium bicarbonate, potassium carbonate, sodium formate, sodium dihydrogenphosphate and disodium hydrogenphosphate.

Treating the dyestuffs according to the invention with the acid-binding agents, with or without heating, bonds the dyes chemically to the cellulose fibers. Especially the dyeings on cellulose, after they have been given the usual aftertreatment of rinsing to remove unfixed dye portions, show excellent properties.

The dyeings of polyurethane and polyamide fibers are customarily carried out from an acid medium. The dyebath may contain for example acetic acid and/or ammonium sulfate and/or acetic acid and ammonium acetate or sodium acetate to bring it to the desired pH. To obtain a dyeing of acceptable levelness it is advisable to add customary leveling auxiliaries, for example based on a reaction product of cyanuric chloride with three times the molar amount of an aminobenzenesulfonic acid or aminonaphthalenesulfonic acid or based on a reaction product of for example stearylamine with ethylene oxide. In general the material to be dyed is introduced into the bath at a temperature of about 40°C and agitated therein for some time, the dyebath is then adjusted to the desired weakly acid, preferably weakly acetic acid, pH, and the actual dyeing is carried out at temperature between 60 and 98°C. However, the dyeings can also be carried out at the boil or at temperatures up to 120°C (under superatmospheric pressure).

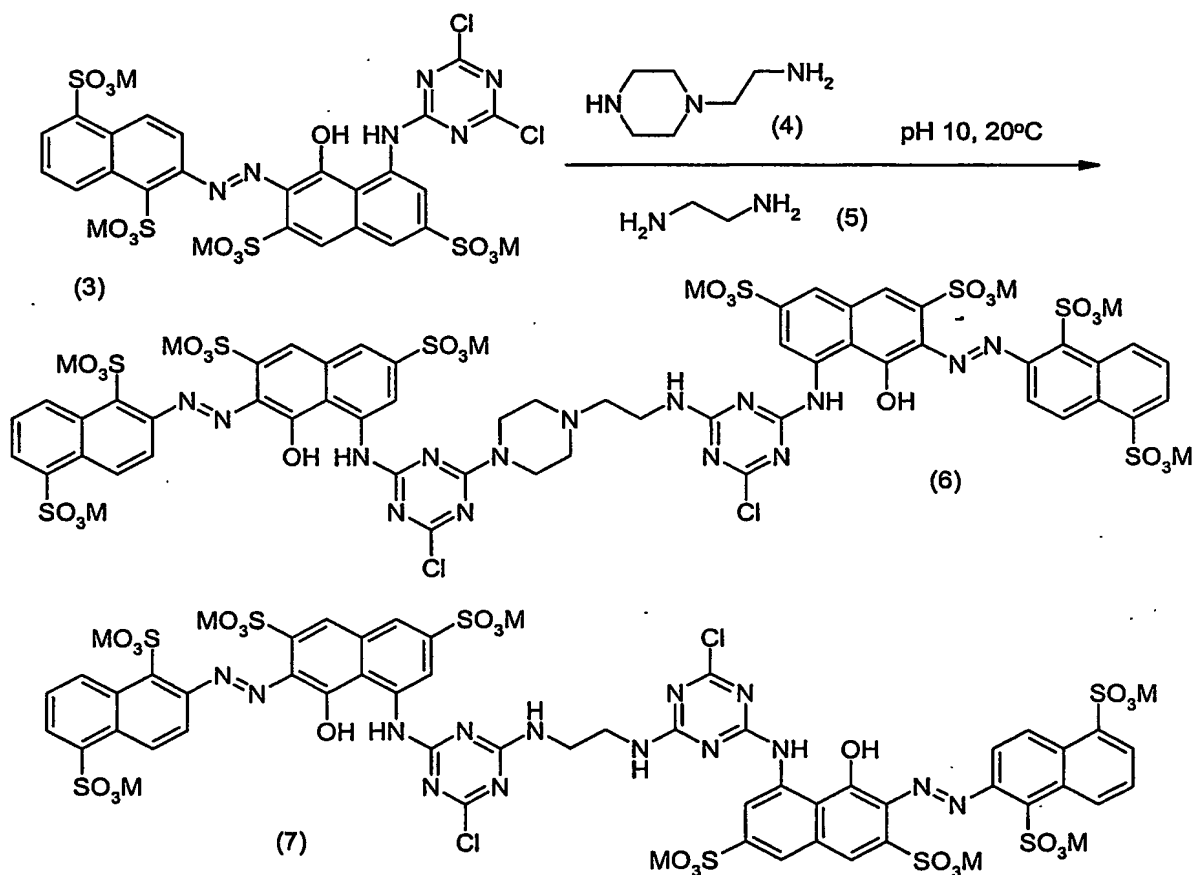
The examples hereinbelow serve to illustrate the invention. Parts and percentages are by weight, unless otherwise stated. Parts by weight relate to parts by volume as the kilogram relates to the liter. The compounds described in the examples in terms of a formula are indicated in the form of the free sulphonic acids, but as in general they are prepared and isolated in the form of their alkali metal salts, such as lithium, sodium or potassium salts, and used for dyeing in the form of these salts. The starting compounds and components mentioned in the form of the free acid in the examples hereinbelow may be used in the synthesis as such or similarly in the form of

their salts, preferably alkali metal salts.

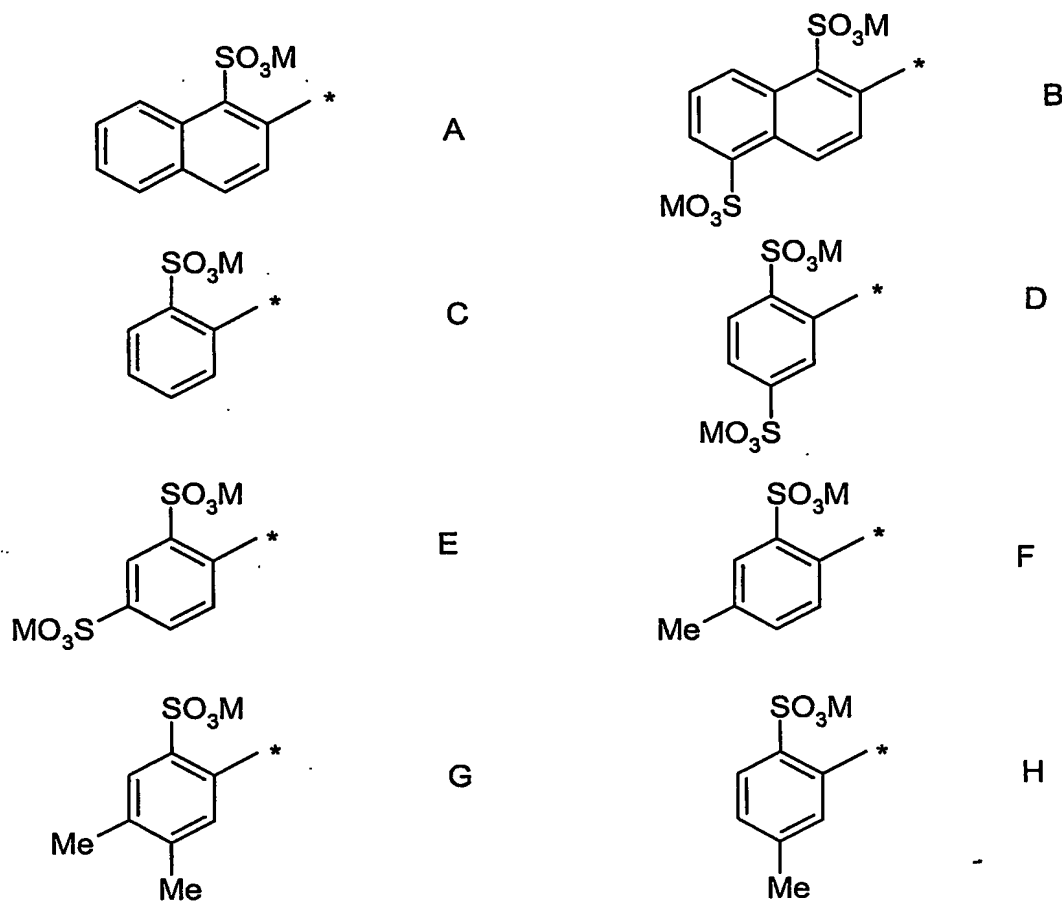
### 5 Example 1

A 1:1 molar mixture of 2-aminoethylpiperazine (4) and ethylenediamine (5) (0.006 mol) was added to a stirred suspension of the dichlorotriazinyl red dye(3) (0.012 mol) in water (350 mols) at pH 6. The pH was adjusted and maintained at pH 10 by the addition of 2N NaOH solution. After three  
10 hours, chromatography indicated that the reaction was complete and the pH was adjusted to 6 with 2N HCl before precipitating the product by addition of methylated spirits. The resulting solid was filtered off and dried to give a dark red powder (11.3g). Analytical data were consistent with a 1:1 mixture of the two dyes (6) and (7).

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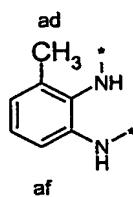
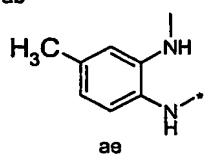
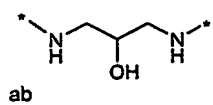
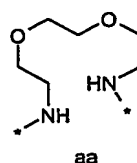
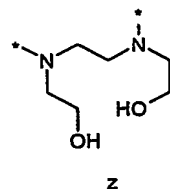
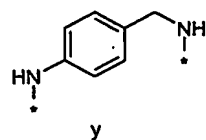
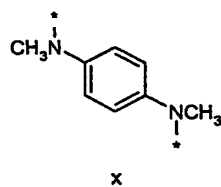
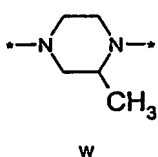
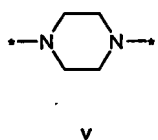
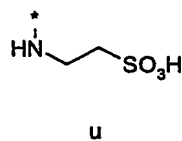
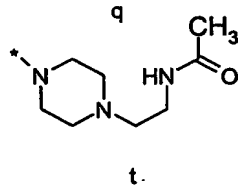
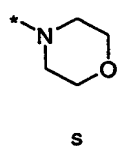
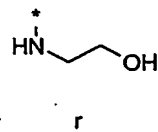
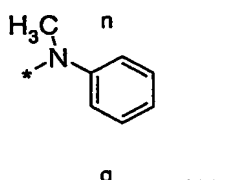
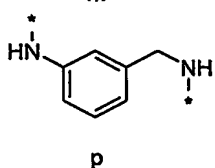
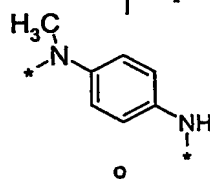
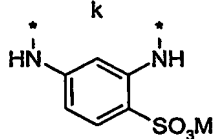
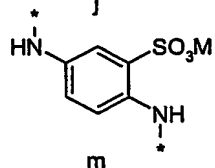
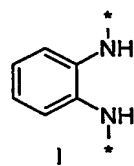
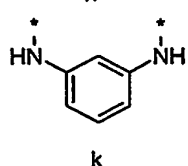
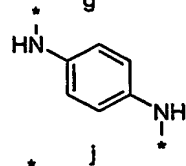
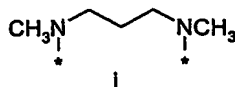
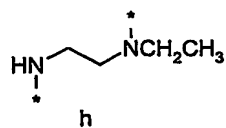
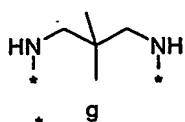
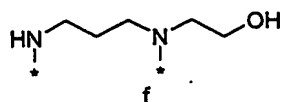
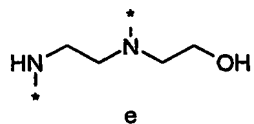
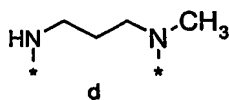
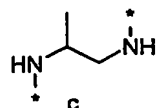
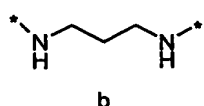
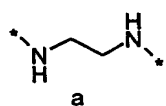


The examples herein below describe further dye mixtures according to the invention. They may be prepared according to the invention either by mechanically mixing the individual dyes or else chemically, for example similarly to the above illustrative embodiment, using as starting compounds of general formula (III), in which X is for example chlorine and Ar<sup>1</sup> and Ar<sup>2</sup> are for example:



10

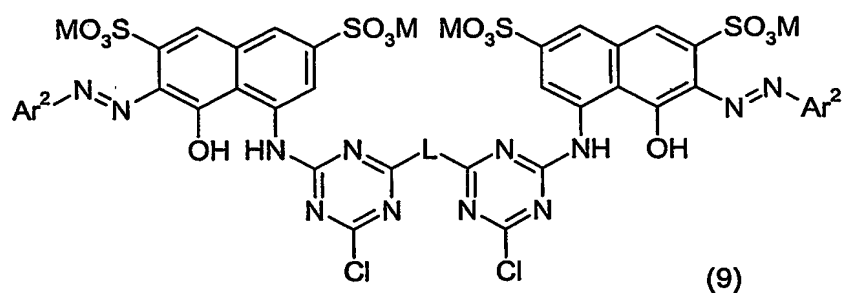
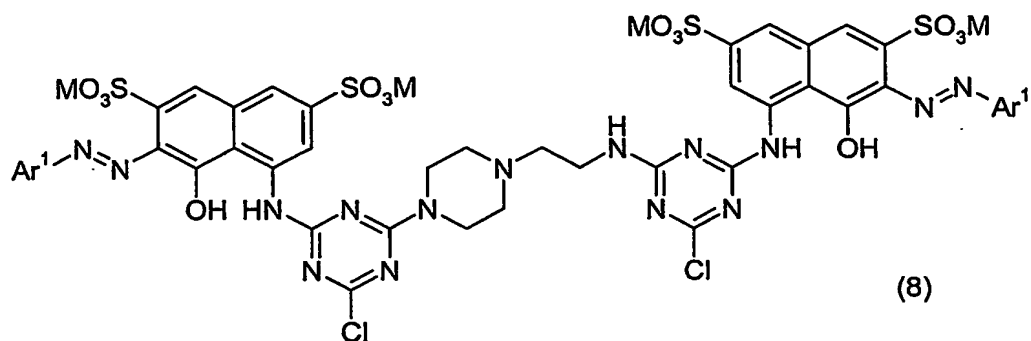
2-aminopiperazine and a diamine H-L-H or amine H-L, wherein L is for example a residue of formula a to af



af

Following exactly analogous procedures the following dyes (examples 2 – 56) were synthesized giving 1:1 mixtures of the respective dyestuff (8) and

5 (9)

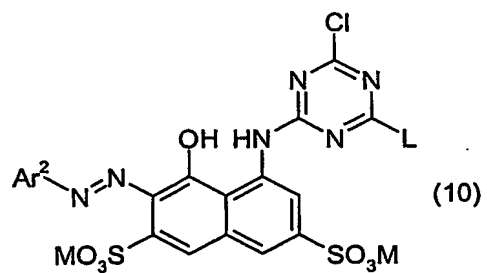


Example No.	Ar <sup>1</sup>	Ar <sup>2</sup>	L
2	A	A	a
3	A	A	b
4	A	A	c
5	A	A	d
6	A	A	e
7	A	A	f
8	A	A	g
9	A	A	h
10	A	A	k
11	A	A	l

Example No.	Ar <sup>1</sup>	Ar <sup>2</sup>	L
12	A	A	p
13	B	B	a
14	B	B	d
15	B	B	g
16	B	B	k
17	B	B	l
18	B	B	m
19	B	B	o
20	B	B	p
21	A	G	j
22	A	G	k
23	A	G	l
24	B	F	k
25	B	F	l
26	B	F	o
27	B	F	p
28	C	C	a
29	C	C	k
30	C	C	l
31	F	F	a
32	F	F	k
33	F	F	l
34	D	D	k
35	D	D	o
36	E	E	l
37	H	H	m
38	H	H	n
39	G	G	l

Example No.	Ar <sup>1</sup>	Ar <sup>2</sup>	L
40	G	G	n
41	B	B	v
42	F	F	v
43	B	B	w
44	F	F	w
45	B	B	x
46	F	F	x
47	B	B	f
48	F	F	y
49	F	F	z
50	B	B	aa
51	B	B	j
52	F	F	j
53	F	F	o
54	A	A	ab
55	B	B	ae
56	B	B	af

Examples 57-71 consist of mixtures of dyes of the form (8) and (10).





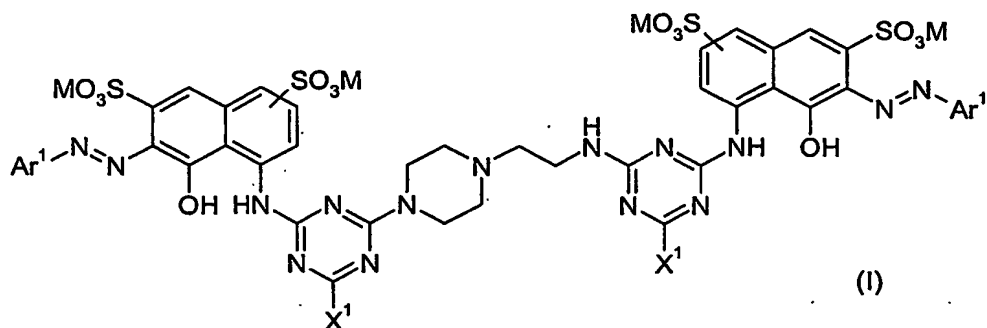
Example No.	Ar <sup>1</sup>	Ar <sup>2</sup>	L
57	A	A	q
58	A	A	r
59	A	A	u
60	A	A	t
61	B	B	q
62	B	B	s
63	B	B	t
64	B	B	u
65	F	F	q
66	F	F	s
67	F	F	t
68	C	C	s
69	C	C	t
70	G	G	u
71	B	B	ad

All these dyestuff mixtures give excellent application properties on cellulose containing material, especially high levels of solubility in water or salt solution, high fixation degrees, ease of washing out the unfixed dyestuff, good fastness to light and water as well as robustness to process variables.

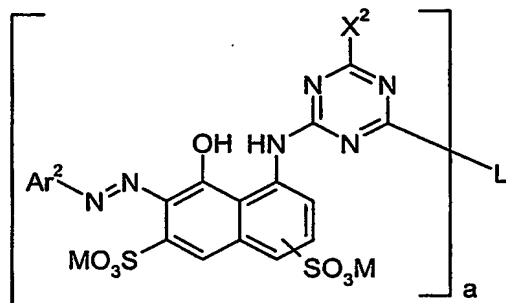
What is claimed is:

1. Mixture of fibre reactive dyes comprising one or more dyestuffs of the formula (I)

5



and one or more dyestuffs of the general formula (II)



10

where

$X^1$ ,  $X^2$  are independently a labile atom or group;

$Ar^1$  is an aromatic residue substituted by at least one  $-SO_3M$  group;

$M$  is hydrogen or alkali metal, especially sodium;

15  $Ar^2$  is an aromatic radical substituted with at least one  $-SO_3M$  group;

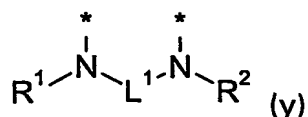
$a$  is 1 or 2

wherein,

if  $a$  is 2

$L$  is a divalent radical typically of the form (y)

20



where

R<sup>1</sup> and R<sup>2</sup> are independently hydrogen, C<sub>1</sub>-C<sub>4</sub> alkyl optionally substituted by -OR, -SR, -SO<sub>3</sub>M or X, or

a phenyl group optionally substituted by a sulfonic acid group, -OR, -C<sub>1</sub>-C<sub>4</sub>-alkyl, or NR'COR and

L<sup>1</sup> is arylene or alkylene optionally substituted by a sulfonic acid group, -OR, -C<sub>1</sub>-C<sub>4</sub>-alkyl - COOR, or NR'COR

or

L is aminoethylpiperazine, under the proviso that if L is aminopiperazine, Ar<sup>1</sup> and Ar<sup>2</sup> are different or

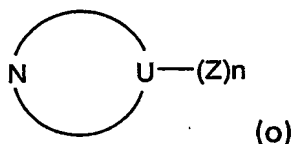
if a is 1

L is a monovalent radical -NR<sup>3</sup>R<sup>4</sup>, -SR<sup>3</sup> or -OR<sup>3</sup>

where

R<sup>3</sup> and R<sup>4</sup> have one of the meanings of R<sup>1</sup> and R<sup>2</sup> or for --

NR<sup>3</sup>R<sup>4</sup>, R<sup>3</sup> and R<sup>4</sup> can form a cyclic structure of the form (o)



where

U is an C<sub>4</sub>-C<sub>6</sub> alkyl residue optionally substituted by a substituent of formula Z and optionally interrupted by heteroatoms or heteroatom-containing groups such as -O-, -NR<sup>1</sup>,

n is 1, 2 or 3 and

Z is hydrogen, optionally substituted C<sub>1</sub>-C<sub>4</sub> alkyl, -OR<sup>5</sup>, -CO<sub>2</sub>R<sup>5</sup>, -COR<sup>5</sup>

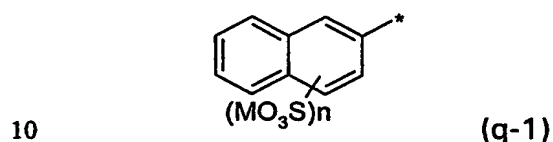
and

$R^5$  is hydrogen, optionally substituted  $C_1$ - $C_4$  alkyl, optionally substituted vinyl, optionally substituted phenyl.

2. Dyestuff mixture according to claim 1

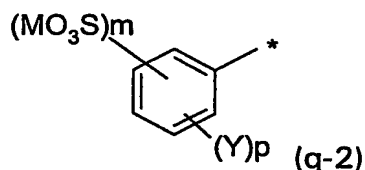
5 wherein

$X^1$  and  $X^2$  is independently chlorine, fluorine or 3 or 4-carboxypyridinium;  
 $Ar^1$  and  $Ar^2$  is independently a naphthyl residue substituted by at least one sulfo group (q-1)



where n is 1 to 3

or is a phenyl residue substituted by at least one sulfo group (q-2)



15 wherein

m is 1 or 2

p is 1 or 2 and

Y is independently hydrogen, halogen,  $R^5$ ,  $OR^5$ ,  $SR^5$ ,  $NHCO R^5$ ,

where  $R^5$  is as given in claim 1.

20

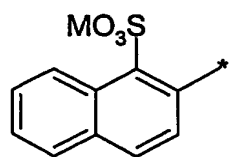
3. Dyestuff mixture according to claim 1

wherein

$X^1$  and  $X^2$  is chlorine;

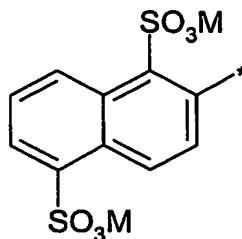
$Ar^1$  and  $Ar^2$  are independently a naphthyl residue of the formula (q-11) or (q-12)

25



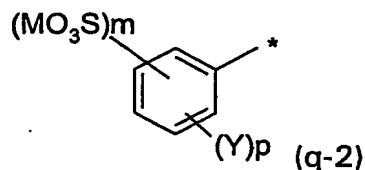
(q-11)

or



(q-12)

or are a phenyl residue substituted by at least one sulfo group (q-2)



wherein

m is 1 or 2

p is 1 or 2 and

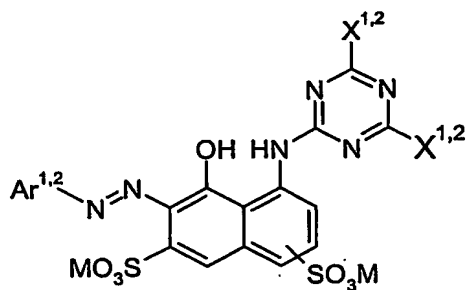
Y is methyl.

4. Dyestuff mixture according to claim 1 wherein a is 1 and L is morpholine.

5. A dye mixture according to at least one of the claims 1 to 4 wherein a dye of formula (I) is present in the mixture in an amount of from 1% by weight to 99% by weight and a dye of the formula (II) is present in the mixture in an amount of from 99% by weight to 1% by weight.

6. A dye mixture according to at least one of the claims 1 to 4 wherein a dye of formula (I) is present in the mixture in an amount of from 10% by weight to 90% by weight and a dye of the formula (II) is present in the mixture in an amount of from 90% by weight to 10% by weight.

7. A process for preparing a dye mixture as claimed in one or more of claims 1 to 5, which comprises reacting chromophores of formula (III)



(III)

wherein Ar<sup>1</sup>, Ar<sup>2</sup>, X<sup>1</sup>, X<sup>2</sup> and M are as defined in claim 1 with an appropriate mixture of 2-aminoethylpiperazine and a diamine H-L-H, or amine H-L, wherein L is as defined above, followed by precipitation using  
5 methylated spirits and conventional filtration.

8. A process for dyeing hydroxy- and/or carboxamido – containing fiber material, in which dyestuffs or dyestuff mixtures are applied to the material and the dyes are fixed to the material by means of heat or with  
10 the aid of an alkali or by means of heat and with the aid of an alkali, which comprises dye mixtures or dyestuffs as claimed in one or more of the claims 1 to 5.

# INTERNATIONAL SEARCH REPORT

Intern application No  
PCT/EP 12271

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 7 C09B67/00

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 C09B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, CHEM ABS Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0 693 538 A (CIBA GEIGY AG) 24 January 1996 (1996-01-24) cited in the application claim 1	1-8
Y	US 5 892 006 A (TZIKAS ATHANASSIOS) 6 April 1999 (1999-04-06) claim 1	1-8
Y	DE 100 64 496 A (DYSTAR TEXTILFARBEN GMBH & CO) 4 July 2002 (2002-07-04) claim 1	1-8
A	WO 99 05244 A (CONNOR DANIEL STEDMAN ;SCHEIBEL JEFFREY JOHN (US); VINSON PHILLIP) 4 February 1999 (1999-02-04) cited in the application claim 1	1-8
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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- \*G\* document member of the same patent family

Date of the actual completion of the international search

25 February 2004

Date of mailing of the international search report

08/03/2004

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## INTERNATIONAL SEARCH REPORT

Internat  
PCT/EP Application No  
/12271

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 00 08104 A (BASF AG ; EBENEZER WARREN JAMES (GB); MYNETT DONNA MARIA (GB)) 17 February 2000 (2000-02-17) cited in the application claim 1 -----	1-8
P,A	WO 02 092697 A (DYSTAR TEXTILFARBEN GMBH & CO ; EBENEZER WARREN JAMES (GB)) 21 November 2002 (2002-11-21) claim 1 -----	1-8
P,A	EP 1 380 621 A (DYSTAR TEXTILFARBEN GMBH & CO) 14 January 2004 (2004-01-14) claim 1 -----	1-8



# INTERNATIONAL SEARCH REPORT

on patent family members

Internat Application No

PCT/EP 12271

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0693538	A	24-01-1996	BR 9502861 A CN 1133323 A , B DE 59509529 D1 EP 0693538 A2 ES 2161847 T3 GR 3036651 T3 JP 8003469 A PT 693538 T US 5631352 A	04-06-1996 16-10-1996 27-09-2001 24-01-1996 16-12-2001 31-12-2001 09-01-1996 30-01-2002 20-05-1997
US 5892006	A	06-04-1999	US 5735911 A US 5612463 A US 5451665 A DE 59108779 D1 DE 59109196 D1 DE 59109201 D1 EP 0478503 A2 EP 0735107 A2 EP 0735113 A2 ES 2106070 T3 ES 2150620 T3 ES 2152455 T3 HK 1001093 A1 JP 3231364 B2 JP 4258674 A JP 3389555 B2 JP 2001026726 A JP 2002194241 A US 5232462 A	07-04-1998 18-03-1997 19-09-1995 21-08-1997 05-10-2000 23-11-2000 01-04-1992 02-10-1996 02-10-1996 01-11-1997 01-12-2000 01-02-2001 22-05-1998 19-11-2001 14-09-1992 24-03-2003 30-01-2001 10-07-2002 03-08-1993
DE 10064496	A	04-07-2002	DE 10064496 A1 BR 0116419 A CA 2428054 A1 WO 02051944 A1 EP 1345994 A1	04-07-2002 30-12-2003 05-05-2003 04-07-2002 24-09-2003
WO 9905244	A	04-02-1999	AU 738353 B2 AU 8124998 A BR 9811524 A CA 2297171 C CN 1270622 T EP 1002031 A1 HU 0002626 A2 WO 9905244 A1 ID 28301 A JP 2001511474 T TR 200000923 T2 US 2002103096 A1 US 6306817 B1 ZA 9806447 A	13-09-2001 16-02-1999 18-12-2001 01-04-2003 18-10-2000 24-05-2000 28-11-2000 04-02-1999 10-05-2001 14-08-2001 21-09-2000 01-08-2002 23-10-2001 21-01-1999
WO 0008104	A	17-02-2000	AT 237661 T BR 9912628 A DE 69906983 D1 DE 69906983 T2 EP 1100847 A1 ES 2197658 T3 WO 0008104 A1	15-05-2003 02-05-2001 22-05-2003 18-12-2003 23-05-2001 01-01-2004 17-02-2000

# INTERNATIONAL SEARCH REPORT

on patent family members

Internat... Application No

PCT/EP.../12271

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 0008104	A	JP 2002522587 T PT 1100847 T TR 200100320 T2 US 6359121 B1	23-07-2002 31-07-2003 21-06-2001 19-03-2002
WO 02092697	A	21-11-2002 CA 2446784 A1 WO 02092697 A1 EP 1387865 A1	21-11-2002 21-11-2002 11-02-2004
EP 1380621	A	14-01-2004 CA 2434825 A1 EP 1380621 A1	10-01-2004 14-01-2004